Electrochemically-induced and Electron Transfer Chain-catalysed Substitution Reactions in Dinuclear Molybdenum Carbonyl Complexes $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\mu\text{-}SR)_2]$ and $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\mu\text{-}SR)_2]^{2+}[A]_2$ (R = Me, Ph; A = BF_4^- or PF_6^-)

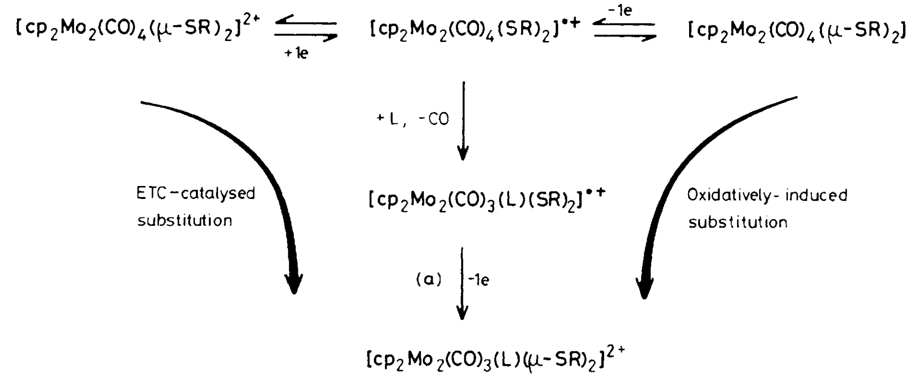
Monique Guéguen, Jacques E. Guerchais, François Y. Pétillon, and Jean Talarmin*

Unité Associée au CNRS No. 322, 'Chimie, électrochimie et photochimie moléculaires', Faculté des Sciences et Techniques, Université de Bretagne Occidentale, 29287 Brest Cedex, France

A radical cation, transiently produced in a single step two-electron transfer, is shown to be the reactive species in a substitution process which can be oxidatively-induced or catalysed *via* an electron transfer chain mechanism.

Recently, we reported on the oxidative electrochemistry of the dimeric molybdenum carbonyl complexes, $[cp_2Mo_2(CO)_4(\mu\text{-}SR)_2]$ (cp = $\eta^5\text{-}C_5H_5$), which undergo a single step, two-electron oxidation. The transfer of two electrons at the same potential is thought to arise from the formation of a metal–metal bond in the product, which stabilizes it with respect to the single-oxidized intermediate.[1,2] Indeed, the two-electron oxidation of the $[cp_2Mo_2(CO)_4(\mu\text{-}SR)_2]$ complexes induces a *cis–trans* isomerization. The presence of a metal–metal bond in the dication is ascertained by comparing the *X*-ray crystal structures of the dication, R = Bu^t [Mo · · · Mo 3.008(2) Å],[1] and of the neutral molecule, R = Ph [Mo · · · Mo 3.940(2) Å].[3] Although the radical cation $[cp_2Mo_2(CO)_4(SR)_2]^{\cdot +}$ is thermodynamically unstable with respect to disproportionation into a neutral compound and a dication, we now show that it is a key intermediate from a kinetic point of view.

The electrochemical two-electron oxidation of the neutral



Scheme 1. Oxidatively-induced and ETC-catalysed substitution of $[\mathrm{cp_2Mo_2(CO)_4(\mu\text{-}SR)_2}]^z$ complexes (z = 0 or + 2). R = Me, Ph; L = MeCN. (a) Reactions (3) and/or (4) (see text).

dimers (R = Me, Ph) in an acetonitrile electrolyte, at the potential of the *trans* → cis^{2+} reaction,[1] results in the formation of a by-product along with the expected dication. The new compound is the major product when the electrolysis is performed at 40 °C. The chemical oxidation of the neutral dimers in MeCN (at 40 °C, R = Ph; at 65 °C, R = Me) by two equiv. of $\mathrm{Ag^+}$ yielded the same complexes as those generated on electrochemical oxidation, as well as other metal species. Analytical, spectral (i.r. and ^{1}H n.m.r.),† and conductimetric data obtained from the electrochemically- or chemically-generated compounds are consistent with the formulation $[\mathrm{cp_2Mo_2(CO)_3(MeCN)(\mu\text{-}SR)_2}]^{2+}[\mathrm{A}]_2$ (A = $\mathrm{BF_4^-}$ or $\mathrm{PF_6^-}$) for these complexes. The substitution of MeCN for CO in the neutral tetracarbonyl dimers is therefore an oxidatively-induced process (Scheme 1). The reduction peak of the substituted dication is irreversible and shifted in the negative direction by *ca.* 0.3 V with respect to the reduction of the tetracarbonyl analogue. The potential shift is consistent with the electron-releasing nature of MeCN as compared with CO.

The electrochemical reduction of the tetracarbonyl dication (R = Me, Ph) in MeCN, at the potential of the $cis^{2+} \rightleftarrows cis$ transition,[1] also produces the substituted dication, $[\mathrm{cp_2Mo_2(CO)_3(MeCN)(\mu\text{-}SR)_2}]^{2+}$ (yield: 51 ± 3%, room temp.) as well as the neutral tetracarbonyl parent (yield: 43 ± 3%, room temp.). The material and charge balances require that other products are present, since about 0.5 F/mol of the tetracarbonyl dication is transferred. However, cyclic voltammetry (c.v.) of the catholyte does not allow the hypothetical products to be detected.

The electrolysis plots, $I_{\mathrm{cell}} = f(t)$ or $I_{\mathrm{cell}} = f(Q)$ (I_{cell}: cell current; Q: charge passed in coulombs) display the convex curvature typically observed[4] when an electron transfer chain[5] (ETC)-catalysed substitution is operative. Several examples of such processes have been recently reported for mononuclear,[6] dinuclear,[7] and polynuclear[4,8] complexes. One of the conditions limiting the generality of ETC processes concerns the lifetime of the paramagnetic species whose degradation generally is the chain-terminating step.[7,8]

In the present case, neither the neutral dimer nor the tetracarbonyl dication undergo substitution under thermal or photochemical activation on the time-scale of the electrochemical experiments. The reactive intermediate of the electrochemically-induced and of the ETC-catalysed substitutions must therefore be a species which is generated both from the oxidation of the neutral complexes and from the reduction of the corresponding dications. This points to the substitution-labile species being a thermodynamically unfavoured (see above) radical cation. Owing to the fact that the unsubstituted complex undergoes a two-electron transfer in a single step, an additional terminating step needs to be considered, *i.e.*, the reduction of the parent radical cation, equation (1).

$$[\mathrm{cp_2Mo_2(CO)_4(SR)_2}]^{\cdot+} + 1\mathrm{e} \longrightarrow [\mathrm{cp_2Mo_2(CO)_4(\mu\text{-}SR)_2}] \tag{1}$$

$$[\mathrm{cp_2Mo_2(CO)_4(SR)_2}]^{\cdot+} + [\mathrm{cp_2Mo_2(CO)_3(MeCN)(SR)_2}]^{\cdot+} \rightleftharpoons [\mathrm{cp_2Mo_2(CO)_4(\mu\text{-}SR)_2}] + [\mathrm{cp_2Mo_2(CO)_3(MeCN)(\mu\text{-}SR)_2}]^{2+} \tag{2}$$

Owing to the relative ease of reduction of the substituted and unsubstituted dications, the electron-transfer to the parent radical cation may occur homogeneously, equation (2). Reactions (1) and/or (2) are likely to be responsible for the production of some neutral dimer in the ETC-catalysed process. The conversion of the substituted radical cation into product may take place according to either of reactions (2), (3), and (4) [Scheme 1, path (a)].

$$[\mathrm{cp_2Mo_2(CO)_3(MeCN)(SR)_2}]^{\cdot+} + [\mathrm{cp_2Mo_2(CO)_4(\mu\text{-}SR)_2}]^{2+} \rightleftharpoons [\mathrm{cp_2Mo_2(CO)_3(MeCN)(\mu\text{-}SR)_2}]^{2+} + [\mathrm{cp_2Mo_2(CO)_4(SR)_2}]^{\cdot+} \tag{3}$$

$$[\mathrm{cp_2Mo_2(CO)_3(MeCN)(SR)_2}]^{\cdot+} - 1\mathrm{e} \rightarrow [\mathrm{cp_2Mo_2(CO)_3(MeCN)(\mu\text{-}SR)_2}]^{2+} \tag{4}$$

The very formation of the substituted dication from the short-lived intermediate $[\mathrm{cp_2Mo_2(CO)_4(SR)_2}]^{\cdot+}$ demonstrates that ligand binding to this species is a fast step since it competes very effectively with a fast electron transfer, equation (1). (In Scheme 1, the possibility that CO loss occurs subsequent to and not concomitant with L binding is not ruled out.)

The substitution reaction may be initiated from the parent dication by the passage of a small amount of electricity corresponding to 0.02 to 0.10 F/mol of the tetracarbonyl dication. The electrolysis is then interrupted which prevents reactions (1) and (4). C.v. monitoring of the course of the reaction demonstrates that the substitution proceeds for several minutes (up to 1 h). Interestingly, the formation of the

---

† $[\mathrm{cp_2Mo_2(CO)_3(MeCN)(SR)_2}][\mathrm{BF_4}]_2$: satisfactory elemental (C, H, N) analyses for R = Ph and Me were obtained; R = Ph: i.r. (MeCN), ν(CO): 2070, 2035 cm^{-1}; ^{1}H n.m.r. ($\mathrm{CD_3NO_2}$, *vs.* $\mathrm{Me_4Si}$): δ 7.60(m), 6.58(s), 6.45(s), 2.07(s); R = Me: i.r. (MeCN), ν(CO): 2060, 2025 cm^{-1}; ^{1}H n.m.r. ($\mathrm{CD_3NO_2}$, *vs.* $\mathrm{Me_4Si}$): δ 6.33(s), 6.16(s), 2.82(s), 2.68(s).

neutral parent is completely suppressed, the only detected product being $[cp_2Mo_2(CO)_3(MeCN)(\mu\text{-}SR)_2]^{2+}$ in 85—95% yield (c.v. measurements). This suggests that the homogeneous electron transfer, reaction (2), does not contribute significantly to the formation of the substituted dication and of the neutral parent. Phrased in another way, in the presence of MeCN, the unsubstituted radical cation (Scheme 1) only exists in the close vicinity of the electrode where it is reduced provided an appropriate potential is applied. To our knowledge, the formation of the same substituted complex according to an oxidatively-induced reaction or to an ETC-catalysed process is as yet unprecedented.

The CNRS (Centre National de la Recherche Scientifique) is acknowledged for financial support.

Received, 5th December 1986; Com. 1739

References

1 J. Courtot-Coupez, M. Guéguen, J. E. Guerchais, F. Y. Pétillon, J. Talarmin, and R. Mercier, *J. Organomet. Chem.*, 1986, **312**, 81.

2 B. Zhuang, J. W. McDonald, F. A. Schultz, and W. E. Newton, *Organometallics*, 1984, **3**, 943; *Inorg. Chim. Acta*, 1985, **99**, L29; J. P. Collman, R. K. Rothrock, R. G. Finke, E. J. Moore, and F. Rose-Munch, *Inorg. Chem.*, 1982, **21**, 146.

3 I. B. Benson, S. D. Killops, S. A. R. Knox, and A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 1980, 1137.

4 A. J. Downard, B. H. Robinson, and J. Simpson, *Organometallics*, 1986, **5**, 1140.

5 R. W. Alder, *J. Chem. Soc., Chem. Commun.*, 1980, 1184; for reviews, see: J. K. Kochi, *J. Organomet. Chem.*, 1986, **300**, 139; J. M. Savéant, *Acc. Chem. Res.*, 1980, **13**, 323.

6 J. W. Hersberger, R. J. Klinger, and J. K. Kochi, *J. Am. Chem. Soc.*, 1982, **104**, 3034; 1983, **105**, 61.

7 E. K. Lhadi, H. Patin, and A. Darchen, *Organometallics*, 1984, **3**, 1128; N. C. Schroeder and R. J. Angelici, *J. Am. Chem. Soc.*, 1986, **108**, 3688; M. Arewgoda, B. H. Robinson, and J. Simpson, *ibid.*, 1983, **105**, 1893.

8 A. Darchen, C. Mahé, and H. Patin, *Nouv. J. Chim.*, 1982, **6**, 539; H. H. Ohst and J. K. Kochi, *J. Am. Chem. Soc.*, 1986, **108**, 2897; *Inorg. Chem.*, 1986, **25**, 2066; M. G. Richmond and J. K. Kochi, *ibid.*, 1986, **25**, 656, 1334; M. I. Bruce, D. C. Kehoe, J. G. Matisons, B. K. Nicholson, P. H. Rieger, and M. L. Williams, *J. Chem. Soc., Chem. Commun.*, 1982, 442.